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An original L-shape, tunable *N*-Heterocyclic Carbene platform for efficient gold(I) catalysis

Yue Tang,[†] Idir Benaïssa,[†] Mathieu Huynh, Laure Vendier, Noël Lugan, Stéphanie Bastin,^{*} Philippe Belmont, Vincent César^{*} and Véronique Michelet^{*}

In memory of Guy Lavigne

Abstract: The synthesis and characterization of original NHC ligands based on an imidazo[1,5-*a*]pyridin-3-ylidene (IPy) scaffold functionalized with a flanking barbituric heterocycle is described as well as their use as tunable ligands for efficient gold-catalyzed C-N, C-O and C-C bonds formations. High activity, regio-, chemo- and stereoselectivities are obtained for hydroelementation and domino processes, underlining the excellent performance (TONs and TOFs) of these IPy-based ligands in gold catalysis. The gold-catalyzed domino reactions of 1,6-enynes give rise to functionalized heterocycles in excellent isolated yields under mild conditions. The efficiency of the NHC gold **5^{Me}** complex is remarkable and mostly arises from a combination of steric protection and stabilization of the cationic Au(I) active species by ligand **1^{Me}**.

Over the last two decades, homogeneous gold catalysis has been recognized as a game changer in modern organic synthesis, due to the opportunity to access high molecular complexity from relatively simple substrates in an atom-economical step.^[1] Monodentate ligands *L* play a major role in tuning the activity, stability, and selectivity of the gold catalysts.^[1,2] Although several families of privileged ligands have emerged such as Buchwald-type dialkyl(*o*-diaryl)phosphines^[3] or *N*-Heterocyclic Carbenes (NHCs),^[4] the quest for new and broad spectrum ligand systems in gold catalysis is still actively pursued. A rational and efficient strategy was recently shown to be the functionalization of Buchwald-type phosphines, either by grafting a basic group to direct the anti-nucleophilic attack of alkynes,^[5] or by introducing a cationic charge to enhance the electrophilicity of the gold center.^[6]

Transposing this approach to NHC chemistry by derivatizing the standard 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) ligand into bulkier and/or functionalized NHCs, met only limited success in gold catalysis, since nitrogen substituents remain too far from the gold center to exert an efficient steric environment.^[7]

The imidazo[1,5-*a*]pyridin-3-ylidene platform (IPy), first disclosed independently by the groups of Lassaletta and Glorius in 2005,^[8] places the R group at the C5 position in close proximity to the metal center as a consequence of the annelation of pyridinyl and imidazolyl rings (Figure 1). It may thus be regarded as the geometrically carbene analogue of Buchwald-type phosphines.^[9] Interestingly, IPy-based ligands and related *N*-fused heterobicyclic carbenes were already coordinated to gold(I) and led to efficient catalytic species in some instances (complexes **A-C**, Figure 1).^[10] In line with our dual interests in the design of functionalized NHCs^[11,12] and the development of new selective gold catalytic systems,^[13] we report herein a novel class of functionalized IPy ligands for gold(I) catalysis, whose C5 position is substituted by an anionic (ligand **1⁻**) or neutral barbituric heterocycle (ligand **1^E**), as well as promising preliminary results in gold-catalyzed hydroelementation and domino processes.

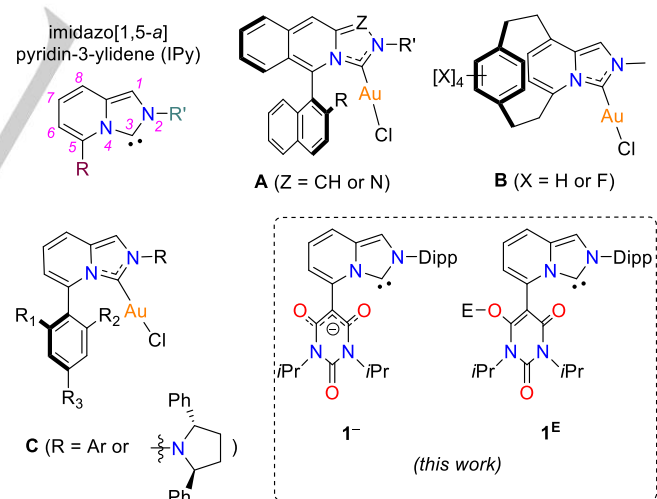


Figure 1. General depiction of the imidazo[1,5-*a*]pyridin-3-ylidene (IPy) platform, *N*-fused heterobicyclic carbene gold(I) complexes **A-C**, and ligand system (**1⁻**, **1^E**). Dipp = 2,6-diisopropylphenyl.

The barbituric heterocycle was chosen as it combines urea and malonate units into its structure, which actually may serve for further derivatization or during catalysis.^[14] The zwitterionic air- and water-stable precursor **1-H** was prepared on gram-scale by reacting [**2-H**]Br with deprotonated hexahydropyrimidinetrione **3** through a facile aromatic nucleophilic substitution (S_NAr) (Scheme 1).^[12] Compound **1-H** was fully characterized by spectroscopic

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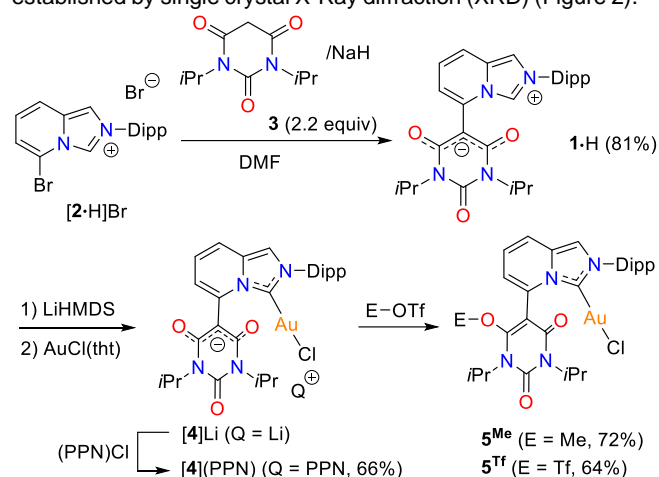
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and analytical techniques and its molecular structure was firmly established by single crystal X-Ray diffraction (XRD) (Figure 2).^[15]



Scheme 1. Synthesis of anionic gold(I) complex **[4](PPN)** and neutral gold(I) complexes **5^{Me}** and **5^{Tf}**. Dipp: 2,6-diisopropylphenyl.

The anionic gold(I) complex $[\text{AuCl}(\mathbf{1})]\text{Li}$ (**[4]Li**) was then cleanly obtained by reacting the stable free NHC **[1]Li** with $\text{AuCl}(\text{tht})$ at low temperature.^[16] For solubility reasons, a salt metathesis was carried out by adding bis(triphenylphosphine)iminium chloride (PPN)Cl to the crude solution of **[4]Li** in CH_2Cl_2 to afford the complex **[4](PPN)** in 66% yield after purification. The molecular structure of **[4](PPN)** was confirmed by an XRD experiment (Figure 2). In order to tune the overall electronic impact of the NHC ligand onto gold center,^[10f,17] complex **[4]Li** was then reacted with methyl triflate or triflic anhydride to furnish the stable, neutral Au(I) complexes **5^{Me}**, and **5^{Tf}**, respectively, in which one oxygen atom of the malonate group is substituted. This O-functionalization of the malonate unit is accompanied by the loss of the symmetry plane present in the anionic complexes **[4](Q)**, as illustrated by the splitting of the signals in the ^1H and ^{13}C NMR spectra of **5^{Me}** and **5^{Tf}**. Additionally, complex **5^{Me}** was characterized by XRD (Figure 2). An in-depth analysis of the topographical steric maps of the ligands in the crystal structures using Cavallo's SambVCA software (Figure 2),^[18,16] reveals that both ligands display high encumbrance over the gold center and even in proximity to the potential binding site in *trans* position to the carbene center (red and orange zones). Such a confinement of gold catalyst was previously shown beneficial for high activity and selectivity.^[7] Additionally, the O-methylation is accompanied by a significant increase of the overall steric pressure of the NHC ligand from $\%V_{\text{bur}} = 47.8$ for $\mathbf{1}^-$ in **[4](PPN)** to $\%V_{\text{bur}} = 53.4$ for $\mathbf{1}^{\text{Me}}$ in **5^{Me}**.

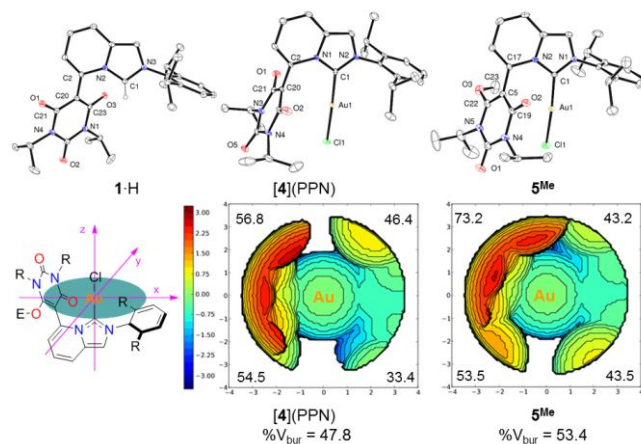
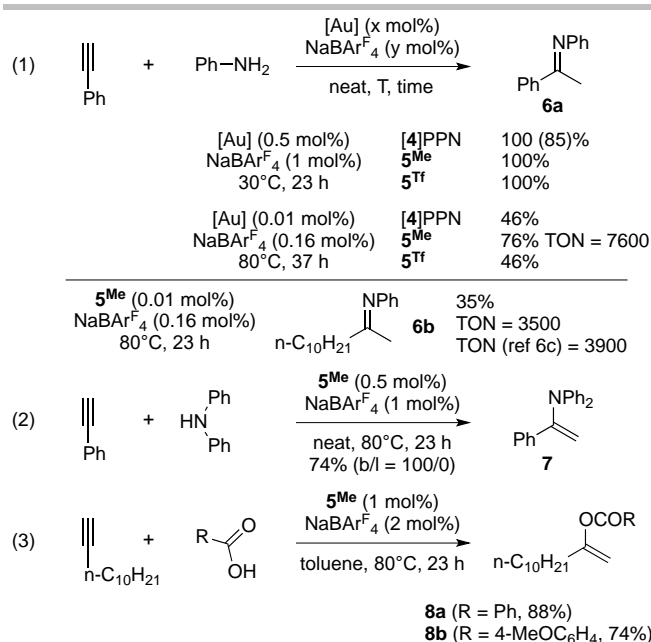


Figure 2. Top: Molecular structures of **1-H** (left), **[4](PPN)** (center), and **5^{Me}** (right) (ellipsoids drawn at 30% probability level). PPN cation and hydrogen atoms have been omitted for clarity. Bottom: Topographical steric maps of **[4](PPN)** (center) and **5^{Me}** (right). Values in the four corners of the maps are the $\%V_{\text{bur}}$ of the NHC ligand in the corresponding quadrant.

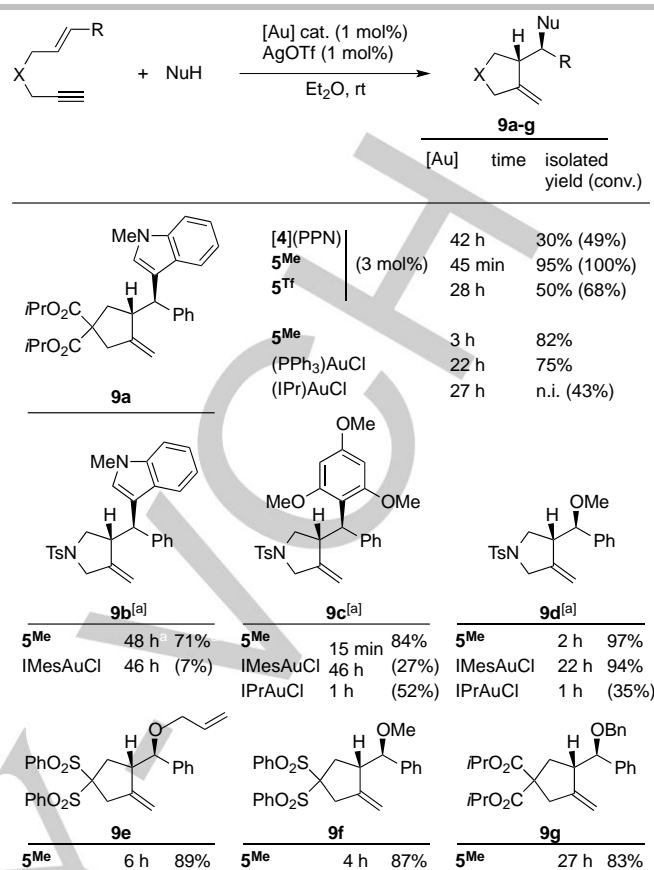
Having the three complexes **[4](PPN)**, **5^{Me}** and **5^{Tf}** in hand, we then evaluated their respective efficiencies in gold(I)-catalyzed hydroamination and cycloisomerization/domino processes. As a first benchmark reaction, we chose the intermolecular hydroamination of terminal alkynes with aniline derivatives,^[19] for which several NHC-Au complexes have shown to be active,^[20] albeit with much less efficiency compared to phosphine-based gold(I) complexes.^[21] Gratifyingly, under neat conditions, the reaction between phenylacetylene and aniline smoothly proceeded to completion at low temperature (30°C) using 0.5 mol% of catalysts **[4](PPN)**, **5^{Me}** or **5^{Tf}** and 1 mol% of $\text{NaBAR}_4^{\text{F}}$ ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{Ph}$) as chloride scavenger (Scheme 2, Eq. 1). At a much lower catalyst loading (0.01 mol%), pre-catalyst **5^{Me}** appeared to be more active than the anionic **[4](PPN)** and **5^{Tf}**, which arises from a fine-tuning of the electronics of the lateral malonate unit for efficient stabilization.^[22] Interestingly, under these conditions, complex **5^{Me}** afforded the imine **6a** in a 76% yield, which corresponds to a catalyst Turn Over Number (TON) of 7600, the highest TON reported so far for a NHC-Au catalyst in hydroamination reaction. Complex **5^{Me}** was also highly active in the hydroamination reaction of a more reluctant substrate such as 1-dodecyne with aniline at 0.01% cat. loading and 80°C showing a TON of 3500 after 23h. This result compares well with L. Zhang's report using an amide-decorated Buchwald-type phosphine system (TON: 3900) under similar conditions.^[5c] These promising results prompted us to investigate the challenging intermolecular addition of secondary anilines onto phenylacetylene, which had been reported only once using 5 mol% of a CAAC-Au(I) system.^[23] Using 0.5 mol% of **5^{Me}** at 80°C, diphenylamine reacted with phenylacetylene to give exclusively the Markovnikov adduct **7** in 74% yield (Scheme 2, Eq. 2).



Scheme 2 Gold-catalyzed intermolecular addition of amine and carboxylic acids to phenylacetylene and 1-dodecyne.

The IPy-Au complexes were then evaluated in the challenging intermolecular addition of carboxylic acids to alkynes (Scheme 2, Eq. 3).^[5c,24] Gratifyingly, while complexes [4](PPN) and 5^{Tf} were inactive, complex 5^{Me} efficiently catalyzed the addition of benzoic acid and 4-methoxybenzoic acid to 1-dodecyne to produce the Markovnikov products **8a-b** in good yields, 88%, and 74%, respectively, with a catalyst loading of only 1 mol%. This is remarkable considering that IPrAuNTf₂ was previously reported inactive under these conditions.^[5c]

The third gold-catalyzed reaction was the atom-economical domino process implying 1,6-enynes and a nucleophile, for which carbon- and oxygen-functionalized nucleophiles are compatible.^[25] These transformations have been described in the presence of phosphine-based ligands as well as NHC-based ligands.^[25,7b] The three complexes [4](PPN), 5^{Me} and 5^{Tf} were firstly evaluated in the case of a carbon-electron rich aromatic indole derivative under standard conditions in diethyl ether at room temperature (Scheme 4, product **9a**). Whereas moderate conversions were observed in the case of complexes [4](PPN) and 5^{Tf}, an excellent isolated yield of 95% was obtained in the case of gold complex 5^{Me} in only 45 minutes with 3 mol% catalyst loading. The lower reactivity of [4](PPN) may be explained by the poor electrophilicity and the lower steric protection of the postulated zwitterionic active species [Au⁺(1⁻)] (see Figure 2), which experimentally evolves towards black nanoparticles, most presumably Au(0) nanoparticles. The lower stability and Lewis acidity, according to Gutmann-Beckett method,^[16] of the gold complexes 5^{Tf} and 5^{Me} may account for the significant difference of activity between both derivatives (50 % vs. 95% yield). The high activity of complex 5^{Me} prompted us to further study its properties in other domino processes and also with a comparison with other NHC-based gold complexes such as IMesAuCl and IPrAuCl (Scheme 3, products **9a-9d**).



Scheme 3. Au-catalyzed domino cyclization/nucleophilic addition of 1,6-enynes with various nucleophiles. [a] in CH₂Cl₂; n.i. not isolated.

In all cases, the efficiency of complex 5^{Me} was outstanding compared to the other NHC-gold complexes in terms of yields, selectivity, or kinetic. The addition of electron-rich indole or 1,3,5-trimethoxybenzene to *N*-tethered 1,6-enyne led efficiently to heterocycles **9b**, and **9c** in 71%, and 84% isolated yields, respectively. Low or moderate conversions were observed in the case of IMesAuCl or IPrAuCl. Moreover, the activity of complex 5^{Me} compared favorably with the activity of pseudo-half-sandwich NHCs bearing *N*-alkylfluorenyl arms.^[7b] The addition of MeOH led to excellent yield for 5^{Me} and IMesAuCl, but a high difference of kinetic for the domino process (Scheme 3, product **9d**) was observed in favor of 5^{Me} complex. The reactivity of carbon-tethered derivatives such as bis-sulfonated 1,6-enynes and diester was also studied and led to very good results as the functionalized alkenes **9e-9g** were isolated in 83-89% yields. The large overall scope is noteworthy since the reaction conditions were amenable with carbon- as well as oxygen-based nucleophiles such as alcohols (allylic alcohol, MeOH, benzylic alcohol). The functionalized heterocycle **9c** was obtained in high yield with TOF = 400 h⁻¹, 8 orders of magnitude higher than with IPrAuCl. Interestingly, in the case of MeOH as nucleophile, the higher efficiency of the gold 5^{Me} complex was again demonstrated as the observed TOF for the synthesis of **9d** was 212 h⁻¹, compared to 35 h⁻¹ in the presence of the standard IPr-based complex (see Supporting Information). With an efficient set of reaction conditions in hand, and considering the much faster conversions with gold complex 5^{Me}, we further challenged the efficiency of the catalyst by conducting the hydroarylation/cyclization reaction on a 1-gram scale (3 mmol) and in the

presence of 0.25 mol% of gold catalyst (see Supporting Information). Remarkably, the heterocycle **9c** was isolated in 87% yield, which corresponds to a decrease in catalyst loading of more than 3 orders of magnitude from this work, and 10 orders of magnitude from previous studies.^[25]

In conclusion, we reported the straightforward and efficient synthesis of new NHC ligands based on an imidazo[1,5-*a*]pyridin-3-ylidene (IPy) scaffold functionalized by a flanking barbituric heterocycle and their use as tunable and efficient NHC ligands for original gold-catalyzed reactions. The efficiency of the related Au(I) complexes was evaluated in C-N, C-O and C-C bonds formation, according to hydroelementation reactions as well as domino processes, with high to excellent TONs and TOFs under optimized conditions. Further studies aiming at a deeper understanding of the key stereoelectronic features of this ligand class,^[26] as well as on the possible transposition of these benefits to other types of transition-metal catalyzed reactions are underway in our laboratories.

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Keywords: *N*-heterocyclic carbene • gold • organometallic complexes • catalysis • atom-economical reactions

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